



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

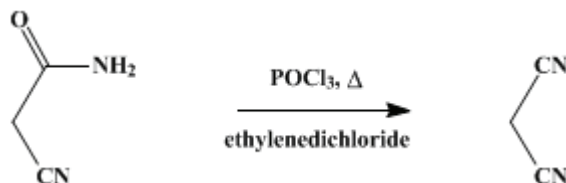
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.535 (1955); Vol. 25, p.63 (1945).

MALONONITRILE



Submitted by Alexander R. Surrey
 Checked by C. F. H. Allen and J. VanAllan.

1. Procedure

In a 12-l. three-necked round-bottomed flask, fitted with a powerful stirrer (Note 1) and a reflux condenser, are placed 1260 g. (15 moles) of cyanoacetamide, 1 kg. of salt (Note 2), and 5 l. of ethylene dichloride. After the mixture has been stirred rapidly for 15 minutes, 800 ml. (8.75 moles) of phosphorus oxychloride is added and the mixture is refluxed for 8 hours in an oil bath (Note 3). After the mixture has been cooled to room temperature, it is filtered and the solid is washed with 500 ml. of ethylene dichloride. The solvent is distilled from the combined filtrates in a 12-l. flask, and the residual crude nitrile is decanted into a 1-l. flask (Note 4) from any solid that may have separated. A fractionating column, condenser, and fractionating receiver are attached, and the malononitrile is distilled under reduced pressure. The fraction boiling at 113–118°/25 mm. weighs 570–654 g. (57–66%) (Note 5). This material may be freed from a small amount of phosphorus oxychloride which is present by redistillation. After a fore-run of about 5 ml., the malononitrile distils smoothly at 92–94°/8 mm.

2. Notes

1. A heavy motor-driven stirrer is advisable, because frequently the solid that separates contains some viscous material that makes stirring difficult.
2. The addition of salt gives a lighter-colored, granular solid that can be easily removed by filtration and washed.
3. The reaction can be done in a hood, or the hydrogen chloride that is evolved can be absorbed in a gas trap.
4. Ground-glass equipment is advisable. The fractionating column is the standard modified Claisen type.
5. The submitter obtained a 70–72% yield at this point in a run of this size and 80% yields in small runs. He also obtained yields of the same order by using a mixture of phosphorus oxychloride and a small amount of phosphorus pentachloride.

3. Discussion

In addition to the methods cited previously,¹ malononitrile has been prepared by the dehydration of cyanoacetamide by phosphorus oxychloride either with salt,² as in the above procedure, or with sodium metabisulfite.³ The vapor-phase reaction of cyanogen chloride and acetonitrile has been patented.⁴

References and Notes

1. *Org. Syntheses Coll. Vol. 2*, 379 (1943).
 2. Surrey, *J. Am. Chem. Soc.*, **65**, 2471 (1943); U. S. pat. 2,389,217 [*C. A.*, **40**, 900 (1946)].
 3. U. S. pat. 2,459,128 [*C. A.*, **43**, 3470 (1949)].
 4. U. S. pat. 2,553,406 [*C. A.*, **45**, 9081 (1951)].
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

sodium metabisulfite

hydrogen chloride (7647-01-0)

acetonitrile (75-05-8)

phosphorus pentachloride (10026-13-8)

ethylene dichloride (107-06-2)

Phosphorus Oxychloride (21295-50-1)

CYANOACETAMIDE (107-91-5)

cyanogen chloride (506-77-4)

Malononitrile (109-77-3)